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SYMMETRY IN CHEMICAL STRUCTURES AND REACTIONS

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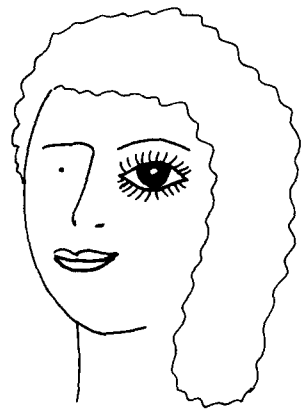
Abstract—Symmetry is analyzed at the atomic level (periodic system, chemical bonding, hybridization), at the molecular level (polyhedral organic molecules and their rearrangement products; isomerism and Polya's theorem; Jahn–Teller effects) and at the supramolecular level (reaction graphs for rearrangements and automerizations; repeating sequences in polymer chains; conservation of orbital symmetry in chemical reactions). A few excursions into mathematics involve solid angles, heuristics of (3, γ)-cages, and visualization of symmetry operations for graphs in three- and four-dimensional Euclidean spaces.

Mottos:

Tiger! Tiger! Burning bright
In the forests of the night,
What immortal hand or eye
Could frame thy fearful symmetry?
W. Blake



An odd-looking girl from Devizes
Had eyes of two different sizes
The one was so small
It was nothing at all
But the other took several prizes.

INTRODUCTION

In order to arrive at an understanding of, and to be able to live in, a crooked world, human reason needs the representation of perfection in the universe; likewise, in order to understand the behaviour of real gases, physico-chemists had first to discover the laws of perfect or ideal gases. Perfection involves, in many cases, higher symmetry than the extant one.

Symmetry may be either fearful (awesome) or beautiful. It is a well-known fact that no human face is exactly symmetrical, yet some symmetry is required for a beautiful or even a normal countenance; this is the meaning of the above limerick. Escher's drawings[1–3] have a haunting, ominous symmetry. The symmetry of a tulip or of a pineapple is beautiful, yet the symmetry of the spider, shark's teeth, the snake, the octopus or the atomic bomb's mushroom appear to us as frightening; we have been conditioned to experience these reactions by biological or cultural heritage. Psychological tests (the "ink blot" butterfly, or the two human profiles versus the flower vase between them) identify such conditioning and constitute clues for diagnosis and treatment.

By contrast, in the serene world of mathematical, physical and chemical sciences, symmetry is always associated with the lofty majesty of the most basic laws. How beautiful is a planar, perfectly hexagonal benzene, an adamantane, or a dodecahedrane molecule! Or, at the supramolecular level, a snowflake! At the intermediate level, let us think about an infinite planar sheet of carbon atoms in graphite, or an infinite lattice of the same atoms in diamond. All properties of these last two materials, so different in strength, electrical conductivity, colour, transparency and price, are due to the different packing symmetry, owing to different types of bonding in the huge molecule which is the crystal in the latter case, or a sheet in the former case: σ bonds in diamond, (σ + π) bonds in graphite.

As Heisenberg had said, "Physicists learned from mathematicians that the symmetry of a problem as a rule produces a conservation law. All the conservation laws that we know in physics [and of course these are important in chemistry also]—the conservation of energy,

momentum, angular momentum, etc.—rest upon fundamental symmetries in the underlying natural law'' (cited from Coulson's paper entitled *Symmetry*[4a]).

Whereas physics deals especially with the abstract symmetries of mathematically formulated laws (either expressing the nature of fundamental particles, or the connection between measurable variables), chemistry deals with both ''palpable'' symmetries of molecules or crystals, and with more abstract symmetries of electronic orbitals or of chemical reactions.

One can discuss symmetry in chemistry at various levels: (a) atomic (symmetry of electronic orbitals and the Periodic Table of Elements; hybridization, molecular geometry, and stereochemistry of organic and inorganic compounds), (b) molecular (symmetry of small numbers of atoms held together by strong covalent bonds; polyhedra, solid angles, and organic or inorganic compounds with polyhedral structures; isomerism and Polya's theorem, Jahn–Teller effect; tunneling), and (c) supramolecular level (symmetry of large collections of atoms which may or may not be bonded by chemical bonds; examples for the former case are polymers, proteins, polynucleotides, silicates; examples for the latter case are various types of molecular crystals such as the ice of the snowflake). Polyhedral viruses or the quaternary structure of proteins also belong here, as do liquid crystals, membranes, bilayers, etc. There is still another type of more abstract symmetry, namely the symmetry of chemical reactions: conservation of orbital symmetry and aromaticity of transition states; valence isomerizations, automerizations, and regular graphs; heuristics of $(3, \gamma)$-cages.

It should be noted that the interface with mathematics and physics is present at all levels (atomic, molecular, supramolecular). From the rich bibliography on symmetry in the physicochemical sciences we list only a few books[5–15].

Crystallographic aspects are presented in this volume in detail by other contributors (Fichter, Mackay, Senechal and Shafranovskii), polymers are discussed by Chujo, symmetry in chemical reactions is analyzed by Pearson, and isomerism is exposed both by Slanina and by Sokolov, while graph-theoretical aspects are contained in the contribution of Hosoya. Therefore, the present selection of topics, which may appear truncated, was imposed by this framework of other contributions and by space limitations. From the preceding listings we shall pick only a few topics.

SYMMETRY AT THE ATOMIC LEVEL: ATOMS, ELECTRONS AND THE PERIODIC SYSTEM

Quantum chemistry is based on quantum mechanics. Heisenberg, Schrödinger, Dirac, Pauli and others assembled the puzzle bits uncovered by Planck, Einstein and Bohr, and formulated the laws governing the behaviour of electrons around atomic nuclei. The quantum numbers and Pauli's Exclusion Principle explain why the electronic configurations around nuclei with $Z = 1$–109 positive charges (by 1984's count†) give rise to periodically similar behaviour *versus* Z.

The principal quantum number $n = 1, 2, 3, 4, 5, 6, 7$ and the secondary quantum number $l = 0, 1, 2, \ldots, n$ (or equivalently expressed by letters s, p, d, . . . , respectively) obey the $(n + l)$ laws according to the Aufbau Principle: electronic orbitals in the ground state of an atom are occupied in the order of increasing $(n + l)$ values; for equal $n + l$ values, the occupancy order is by increasing n values. These simple laws explain naturally the beautiful symmetry of Mendeleev's Periodic Table of Elements, which is puzzling at first glance (Fig. 1) because some inner shells become filled later (d- or f-type orbitals) and because the periodicity is geared according to completion of p-type orbitals. The ''atomic magic numbers of electrons'' (in opposition to the nuclear magic numbers of nucleons) are $Z_0 = 2, 10, 18, 36, 54, 86, (118)$, i.e. the atomic numbers of the six elements (rare gases) which may exist as free atoms in condensed state: these are the only elements which satisfy simultaneously the electrons' requirement for closed electronic shells, and the urge of the nucleus to group around it Z electrons for attaining electrical neutrality. A simple formula[16] for the ''magic number Z_0 of the rare gases'' is

$$Z_0 = n[(n + 3)^2 + 5]/6 - (n + 2)[1 - (-1)^n]/4.$$

†We look forward to hearing Tom Lehrer's reaction when the news about the IUPAC naming of elements with $Z \geq 104$ will come to Harvard!

Fig. 1. The Aufbau principle explaining the periodic system of elements; if one ignores the small irregularity of 5d and 6d elements at the beginning of the lanthanide and actinide series, one can note the symmetry in filling sequentially the orbitals: *s*; *s*; *p*, *s*; *p*, *s*; *d*, *p*, *s*; *d*, *p*, *s*; *f*, *d*, *p*, *s*; *f*, *d*, *p*, *s*.

n = 1	2	3	4	5	6	7	Z : Element
s							1,2 : H, He
	s						3,4 : Li, Be
	p						5–10 : B–Ne
		s					11,12 : Na, Mg
		p					13–18 : Al–Ar
			s				19,20 : K, Ca
		d					21–30 : Sc–Zn
			p				31–36 : Ga–Kr
				s			37,38 : Rb, Sr
			d				39–48 : Y–Cd
				p			49–54 : In–Xe
					s		55,56 : Cs, Ba
			f				58–71 : Ce–Lu (lanthanides)
				d			57,72–80 : La, Hf–Hg
					p		81–86 : Tl–Rn
						s	87,88 : Fr, Ra
				f			90–103 : Th–Lw (actinides)
					d		89,104–112 : Ac, 104–112

For comparison, the general formula[16] of the nuclear magic numbers ξ_0 is

$$\xi_0 = n(n^2 + 5)/3$$

for any $n > 3$; for $n \leqslant 3$ one has to introduce an additional term, $+n(n - 1)$.

The data of Fig. 1 are obtained immediately, taking into account that each atom may contain at most 1, 3, 5, and 7 s, p, d, and f-type orbitals, respectively, and that according to Pauli's principle, one orbital is filled with two electrons.

In all the other 103 elements, a compromise must be reached by the nucleus and the electrons. This compromise is called "chemical bonding"; therefore all these 103 elements exist (as such or combined with other elements) in their ground states as condensed matter, in chemically bonded forms. Ionic, covalent or metallic bonds are the most common types of bonding.

The symmetry of molecular orbitals is closely connected with the symmetry of atomic orbitals: s-orbitals have spherical symmetry, p-orbitals have reflection symmetry with respect to the three planes determined by the cartesian coordinates, and d- and f-orbitals have more elaborate symmetries. The sign of the wave function ψ changes on traversing a nodal surface: there are $n - 1$ nodal surfaces for orbitals with the principal quantum number n. The probability of finding an electron at a given point is $|\psi|^2$.

Covalent bonds, formed by two atoms having one electron each in a "jointly owned molecular orbital" are of σ type (cylindrical symmetry around the bonding axis) if the overlap between atomic orbitals (AOs) is frontal, or π type if the overlap is lateral (Fig. 2).

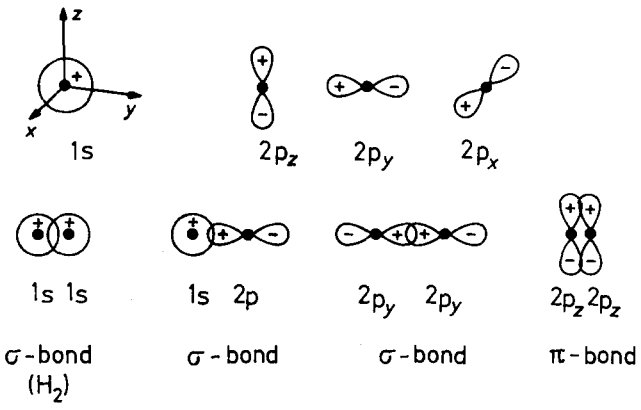


Fig. 2.

Pauling[17] introduced the idea of hybridization of AOs in order to account for molecular geometries. A tetracovalent carbon atom (as in methane or diamond) does not form one bond of one type and three of another type, but four equivalent bonds with sp^3 hybridization, oriented towards the corners of a tetrahedron having the carbon atom in its centre. The normal bond angle is 109.5°. A tricoordinated carbon atom as in ethene, benzene or graphite forms three equivalent sp^2-hybridized σ bonds at 120° and a fourth, weaker π bond using the nonhybridized $2p_z$ AO. A dicoordinated carbon atom as in acetylene forms two sp-hybridized σ bonds at 180° and two π bonds using the remaining nonhybridized 2p orbitals. Of course, the idea of tetrahedral carbon atoms explains the stereochemistry of organic compounds, following Van't Hoff and Le Bel.

One should stress the fact that it is symmetry, and symmetry alone, which makes the distinction between σ and π electrons. This distinction plays a fundamental role in organic chemistry because the σ bonds, with their cylindrical symmetry, ordinarily allow an easy rotation around the bonds at room temperature, whereas the π bonds under the same conditions do not allow such rotations and hence give rise to one type of stereoisomerism called diastereoisomerism or *cis–trans* isomerism. The second type of stereoisomerism, called enantiomerism, appears when a molecule is not superimposable on its mirror image; a common type of such isomerism appears in organic compounds having a chirotopic and stereogenic carbon atom[18], i.e. a carbon atom bonded to four different atoms or groups of atoms[19]. Such molecules are also called chiral. Most of their properties are identical, but they interact differently with polarized light or with other chiral molecules.

The geometries of molecules centered around heavier atoms possessing d orbitals can be similarly understood: trigonal bipyramids with 5-coordination around phosphorus(V) atoms; octahedral symmetry around many 6-coordinated transition metals or sulphur(VI) atoms. Gillespie's rules VSEPR[20] explain the geometry and symmetry of many chemical compounds by postulating various degrees of repulsion between electron pairs in shared MOs or nonshared AOs. Of course, the stereoisomerism of such 5- or 6-coordinated compounds is richer than that of the tetrahedrally 4-coordinated carbon, silicon or nitrogen compounds: whereas an asymmetric 4-coordinated atom (such as carbon, or ammonium nitrogen) gives rise to one pair of enantiomers, for trigonal bipyramids with 5 different ligands there exist 10 pairs of enantiomers, and for octahedral molecules with 6 different ligands there exist 15 pairs of enantiomers. If bidentate or tridentate ligands replace 2 or 3 unidentate ligands, then the number of stereoisomers may be smaller owing to steric strain[21–23].

The importance of stereochemical ideas is attested by the fact that both Van't Hoff (1901) and Werner (1913) were awarded the Nobel Prize at the beginning of this century, and that more recently Barton and Prelog (1976) attained the same distinction for contributions to stereochemistry.

During recent years, the presence of molecular chirality (either due to stereogenic atoms or to hindered rotation) is easily tested in racemic mixtures by nuclear magnetic resonance in molecules possessing diastereotopic groups, as indicated by Mislow[18].

Recently, Mislow and Siegel reformulated in mathematically rigorous form the conditions for chirality[18].

A rich bibliography exists on stereochemistry; only a few recent books are highlighted [24–43].

SYMMETRY AT THE MOLECULAR LEVEL: POLYHEDRA, SOLID ANGLES AND CHEMISTRY

The five regular polyhedra, whose faces are all a single type of regular polygons (n-gons) have fascinated the human imagination since Theaetetus, Euclid, Pappus, Platon and Kepler assigned them a transcendental significance; the latter associated them with the ancient "elements" (fire, air, water, earth and the universe) and with the planets known at that time. One of the reasons for this fascination was the fact that unlike the infinity of regular polygons, there exist only five Platonic solids and three regular plane tesselations (6 triangles, 4 squares, or 3 hexagons meeting at a vertex), which can be considered as polyhedra having an infinite curvature radius. Another reason is their exquisite symmetry, approaching that of the sphere.

One can calculate in sterradians the solid angle 2θ at a vertex of each regular polyhedron according to the following formula[44] for a trihedral solid angle formed from three planar angles $2\alpha_1$, $2\alpha_2$, $2\alpha_3$:

$$\cos\theta = \left(\sum_{i=1}^{3} \cos^2\alpha_i - 1\right) \Big/ 2\prod_{i=1}^{3} \cos\alpha_i.$$

Alternatively, the formula for 2θ may be given in terms of the three dihedral angles, φ_1 to φ_3, between the faces:

$$2\theta = \varphi_1 + \varphi_2 + \varphi_3 - \pi.$$

For the maximal solid angle 2θ formed by four planar angles $2\alpha_i$ (i = 1–4) meeting at a vertex, the formula is

$$\cos\theta = \left(2 - \sum_{i=1}^{4} \sin^2\alpha_i - 2\prod_{i=1}^{4} \sin\alpha_i\right) \Big/ 2\prod_{i=1}^{4} \cos\alpha_i.$$

Among all trigonal pyramids **A** having as base an equilateral triangle, the regular tetrahedron has the smallest sum of solid angles; among all tetrahedra **B** having four equal isosceles triangles as faces, the regular tetrahedron where the faces become equilateral triangles has the largest sum of solid angles (Fig. 3).

For regular polyhedra, all planar angles $2\alpha = (n - 2)/n$ are equal; when the degree of each vertex (number of edges meeting at that vertex) is d, the maximal solid angle $2\theta_d$ is given by

$$2\theta_d = 2\pi - 2d \arccos \frac{\cos(\pi/d)}{\sin(\pi/n)}.$$

For $d = 3$, $\cos\theta_3 = (2 - 3\sin^2\alpha)/2\cos^3\alpha$, i.e. a rigid trihedral solid angle with no degree of freedom allowed. In all subsequent cases the maximal solid angle 2θ formed by d planar angles α is

$$\sin(\theta_4/2) = tg^2\alpha,$$
$$\cos\theta_4 = (2 - 4\sin^2\alpha - 2\sin^4\alpha)/2\cos^4\alpha,$$
$$\cos\theta_5 = [2 - 5\sin^2\alpha - (5 + 5\sqrt{5})\sin^4(\alpha/2)]/2\cos^5\alpha,$$
$$\cos\theta_6 = (2 - 6\sin^2\alpha - 21\sin^4\alpha - 2\sin^6\alpha)/2\cos^6\alpha.$$

According to the value of the solid angle the following order of regular polyhedra may be established (after each polyhedron, the solid angle is given both in sterradians and in the more usual sexagesimal degrees for comparison): tetrahedron (0.5513, 31° 35′); octahedron (1.3593, 77° 53′) cube or hexahedron (1.5708, 90°); icosahedron (2.635, 150° 58′); and dodecahedron (2.96, 169° 41′). This is the order of increasing "perfection," in agreement with the order of increasing numbers of vertices, or of increasing ratios between the radii of inscribed or circumscribed spheres and the length of the edge, or of the angle between an edge and the corresponding

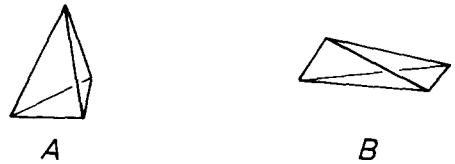


Fig. 3.

radius of the circumscribed sphere. Curiously, the names of the Platonic solids are derived from the number of faces, which is the only parameter varying in a different order for the two reciprocal (dual) pairs: cube–octahedron, and icosahedron–dodecahedron.

In addition to the five Platonic regular polyhedra, there exist semiregular polyhedra having at each vertex more than one type of regular polygon; to this class belong the infinity of prisms and antiprisms, and the 13 Archimedean solids which so far have attracted less attention from organic chemists, but are important for inorganic, particularly silicate, chemistry.

The synthesis of hydrocarbons having the skeletons of Platonic solids with degree 3 (tetrahedrane, cubane and dodecahedrane) has been an interesting challenge during the last 20 years. Owing to steric strain, tetrahedrane $(CH)_4$ is too elusive to be isolated, like its valence isomers cyclobutadiene. However, the same two hydrocarbons become stable when they bear four tertiary-butyl groups, as demonstrated by Maier and his coworkers[45]. This stabilization is due to a "straight-lace effect," due to the high steric constraints imposed by the bulky *t*-butyl groups.

Cubane [$(CH)_8$, Fig. 4(**1**)] was synthetized by Eaton[46]. It was shown that it undergoes interesting transition metal–ion-catalyzed rearrangements yielding either cuneane [Fig. 4(**2**)] with Ag(I) or the *syn*-cyclobutadiene dimer [Fig. 4(**3**)] with Rh(III)[47]. As will be seen in a later section, such rearrangements are symmetry-forbidden as thermal reactions because they involve the concerted migration of four electrons (indicated by distinct lines in the formulas).

Dodecahedrane $(CH)_{20}$ was obtained after considerable effort by Paquette and coworkers[48]. It has an unusually high melting point for a hydrocarbon. Dodecahedrane can also be obtained *via* metal–ion-catalyzed isomerizations[50]. In Paquette's words:

> Little did Plato realize in 400–350 B.C. when he composed his *Timaeus* that the most complex of the five regular polyhedra described therein was to evolve as a major synthetic challenge of organic chemistry later in the 20th century.

Pentaprismane $(CH)_{10}$ was synthesized by Eaton via an elaborated synthesis[50]; benzprismane (triprismane) is very strained[51], yet its isomerization to benzene has a sizable activation barrier owing to the thermally forbidden character of this isomerization.

It will be of interest to synthesize other polyhedral molecules, e.g.the semiregular solids with vertex degrees 3 (valence isomers of annulenes) such as the truncated tetrahedron [Fig. 5(a)-(**4**)] (the faces are 3- and 6-membered rings), the truncated octahedron (**5**) (4- and 6-membered rings), the isomeric, more strained truncated cube (**6**) (3- and 8-membered rings), or the truncated cuboctahedron (**7**); unlike the previous polyhedra (**4**)–(**6**) which each have two types of regular polygonal faces, the last one (**7**) has three types of faces: 4-, 6-, and 8-gons. Other polyhedral molecules which are neither regular nor semiregular polyhedra, such as Fig. 5(b)-(**8**), $(CH)_{16}$, are also interesting [(**8**) has 4- and 5-membered rings].

One should also note that there exist polyhedral molecular skeletons in which one edge of a regular polyhedron corresponds to a chain of two or more covalent bonds. Thus the very stable adamantane or hexamethylenetetramine molecules are regular tetrahedra with edges replaced by a chain of two $CH–CH_2–CH$ or $N–CH_2–N$ bonds, respectively. Schleyer[52] discovered that adamantane [Fig. 5(c)-(**9**)] is the "bottom of the potential energy pit" and is therefore formed by isomerization under the catalytic action of $AlCl_3$ or Rh(I) from any $C_{10}H_{16}$ hydrocarbon; likewise $C_{11}H_{18}$ hydrocarbons yield 1-methyladamantane[53], $C_{14}H_{20}$ hydrocarbons yield diamantane (**10**)[54], and so on for other "inhabitants of Adamantaneland." The graph-theoretical systematic enumeration of polymantanes was published by Balaban and Schleyer[55].

After organic-chemical counterparts of polyhedra, we shall now discuss highly symmetrical inorganic or elemento-organic molecules with polyhedral skeletons. Although 12 carbon atoms

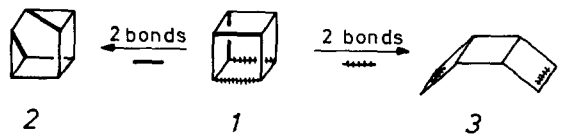


Fig. 4.

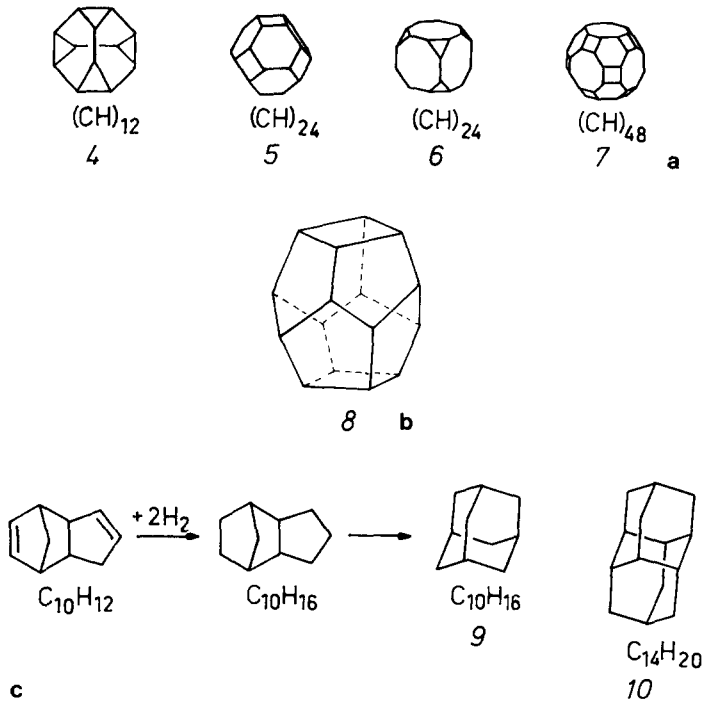


Fig. 5.

cannot be grouped together as icosahedra, boron atoms can; the dodecahedrane anion $(BH)_{12}^{2-}$ is extremely stable. By replacing two BH by CH groups, one can obtain neutral carboranes[56] which preserve their icosahedral skeleton; they exist in three isomeric forms with the two CH groups adjacent, once removed or twice removed. They are quite stable and undergo a variety of substitutions, and therefore they may be regarded as representatives of tridimensional aromatic molecules. The bonding in such electron-deficient systems is different from normal covalent bonds where a line symbolizes a shared electron pair. In boranes there exist two-electron three-centre bonds. Topological rules for the borane structure were developed by Lipscomb[57]. The bonding in polyhedral boranes was investigated, using quantum calculations, by Lipscomb and Hoffmann[58], and using graph-theoretical methods by King and Rouvray[59] and by Balaban and Rouvray[60].

ISOMERISM AND PÓLYA'S THEOREM

Molecules with the same composition (i.e. the same molecular formula) but with different structures (i.e. different arrangements of atoms) are isomeric. Constitutional isomerism is given by different skeletons or adjacencies; stereoisomerism is either enantiomerism (mirror-image nonsuperposability) or diastereomerism. Mislow[61] proposed a different dichotomy based on the isometric operations (identity of scalar properties I_1, or mirror reflection I_2). One thus groups isometric structures (homomers and enantiomers differing by I_1 or I_2) distinctly from anisometric structures which have neither I_1 nor I_2 operations, and which are represented by diastereomers and by constitutional isomers.

Both constitutional and sterical isomerism depend on the symmetry operations of the molecular frame, as shown by Pólya[62] who discovered his famous theorem: the isomer-counting series is obtained by substituting in the symmetry expression (cycle index) the figure-counting series.

It is simple to explain Pólya's theorem by a few examples. The benzene molecule is a planar regular hexagon whose symmetry operations (rotations about proper axes) are represented by the cycle index

$$Z(D_6) = (x_1^6 + 2x_6 + 2x_3^2 + 3x_1^2x_2^2 + 4x_2^3)/12. \quad (1)$$

The formula is obtained on the basis of the character table for benzene, D_{6h}, where only the proper axes are taken into account: $I(x_1^6)$, $2C_6(2x_6)$, $2C_3(2x_3^2)$, $C_6^3 \equiv C_2''(x_2^3)$, $3C_2(3x_2^3$ for the three in-plane axes bisecting two opposite bonds), $3C_2'(3x_1^2x_2^2$ for the three in-plane axes through two opposite atoms). The C_6, C_6^3 and C_3 axes are perpendicular to the plane of the molecule.

For obtaining the numbers of isomers with one type of substituent (e.g. the numbers of mono-, di-, and trichlorobenzenes) the figure-counting series to be substituted in the above formula (1) is

$$x_i = r^i + s^i. \tag{2}$$

By simple algebraic manipulations we obtain the isomer-counting series (ICS) (only constitutional isomerism is involved here because of the planarity due to sp^2-hybridization of the six carbon atoms)

$$\mathrm{ICS}(D_6) = (r^6 + s^6) + (r^5s + rs^5) + 3(r^2s^4 + r^4s^2) + 3(r^3s^3). \tag{3}$$

The coefficients indicate the numbers of isomers, namely one nonsubstituted or hexasubstituted, one mono- or pentasubstituted, three di- or tetrasubstituted, and three trisubstituted benzenes.

Similarly, for benzene substituted with two types of halogen, say chloro-bromobenzene, the figure-counting series is

$$x_i = r^i + s^i + t^i, \tag{4}$$

leading to ICS terms such as $3rst^4$, $3r^2s^4$, $6rs^2t^3$, $11r^2s^2t^2$, etc., which indicate that there are 6 bromodichlorobenzenes, and 11 dibromodichlorobenzenes.

If two labels can be attached to the same atom, as in isotopically carbon- and hydrogen-labelled benzenes, the figure-counting series is[63]

$$x_i = r^i + s^i + r^is^i + t^i, \tag{5}$$

leading to such ICS terms as $3r^2s^4$, $4rst^4$, $9rs^2t^3$, $12rs^3t^2$, $24r^2s^2t^2$, etc., which indicate that there are four isomers of $^{13}C^{12}C_5\ ^2H^1H_5$, etc.

Similarly, for carbon-labelled toluene PhMe

$$Z(\mathrm{PhMe} - {}^*\mathrm{C}) = (x_1^7 + x_1^3x_2^2)/2, \tag{6}$$

because in addition to the identity operation (x_1^7) we have one proper in-plane binary axis passing through three atoms ($x_1^3x_2^2$). The result is the isomer-counting series by substituting (2) into (6):

$$\mathrm{ICS}(\mathrm{PhMe} - {}^*\mathrm{C}) = r^7 + 5r^6s + 16r^5s^2 + 21r^4s^3 + \cdots, \tag{7}$$

indicating that there exist 5 constitutional isomers of toluene labeled with one ^{13}C atom, 16 with two ^{13}C atoms, etc. When, however, we wish to enumerate hydrogen-labelled toluenes or the chlorotoluenes, the cycle index must take into account the free rotation of the methyl group. This is done by multiplying the symmetry groups of the three methyl and five phenyl hydrogens:

$$Z(B)Z(S_3) = \frac{x_1^5 + x_1x_2^2}{2} \cdot \frac{x_1^3 + 3x_1x_2 + 2x_3}{6} =$$
$$= (x_1^8 + 3x_1^6x_2 + 2x_1^5x_3 + x_1^4x_2^2 + 3x_1^2x_2^2 + 2x_1x_2^2x_3)/12. \tag{8}$$

On substituting the figure-counting series (2) we obtain the counting polynomial

$$\mathrm{ICS}(\mathrm{PhMe} - {}^*\mathrm{H}) = r^8 + 4(rs^7 + r^7s) + 10(r^2s^6 + r^6s^2) + 16(r^3s^5 + r^5s^3) + \cdots.$$

Cycloalkanes present stereoisomerism, in addition to constitutional isomerism. We shall illustrate the problem by examining hydrogen-labelled or chlorine-substituted cyclopropane. Three different graphs must be considered[64]. For all isomers, including stereoisomers, one has to consider the prism-like geometry Fig. 6(a)-(**11**); for counting only constitutional and geometrical (*E*/*Z* or diastereoisomers) by ignoring enantiomerism, one has to consider a "planar" system (**12**); finally, for counting only constitutional isomers, one has to consider the symmetry of (**13**) (these $2m$-membered cubic graphs, wherein each vertex is connected to the two vertices adjacent to its opposite vertex, were called Balaban graphs by Mallion[65a]).

Cycle indices and isomer-counting series are (note that Z(**12**) and (1) are identical):

$$Z(\mathbf{11}) = (x_1^6 + 2x_3^2 + 3x_2^3)/6,$$

$$\mathrm{ICS}(\mathbf{11}) = r^6 + r^5s + 4r^2s^4 + 4r^3s^3 + \cdots,$$

$$Z(\mathbf{12}) = (x_1^6 + 2x_3^2 + 4x_2^3 + 3x_1^2x_2^2 + 2x_6)/12,$$

$$\mathrm{ICS}(\mathbf{12}) = r^6 + r^5s + 3r^2s^4 + 3r^3s^3 + \cdots,$$

$$Z(\mathbf{13}) = (x_1^6 + 8x_3^2 + 7x_2^3 + 9x_1^2x_2^2 + 8x_6 + 3x_1^4x_2 + 6x_1^2x_4)/48,$$

$$\mathrm{ICS}(\mathbf{13}) = r^6 + r^5s + 2r^2s^4 + 2r^3s^3 + \cdots.$$

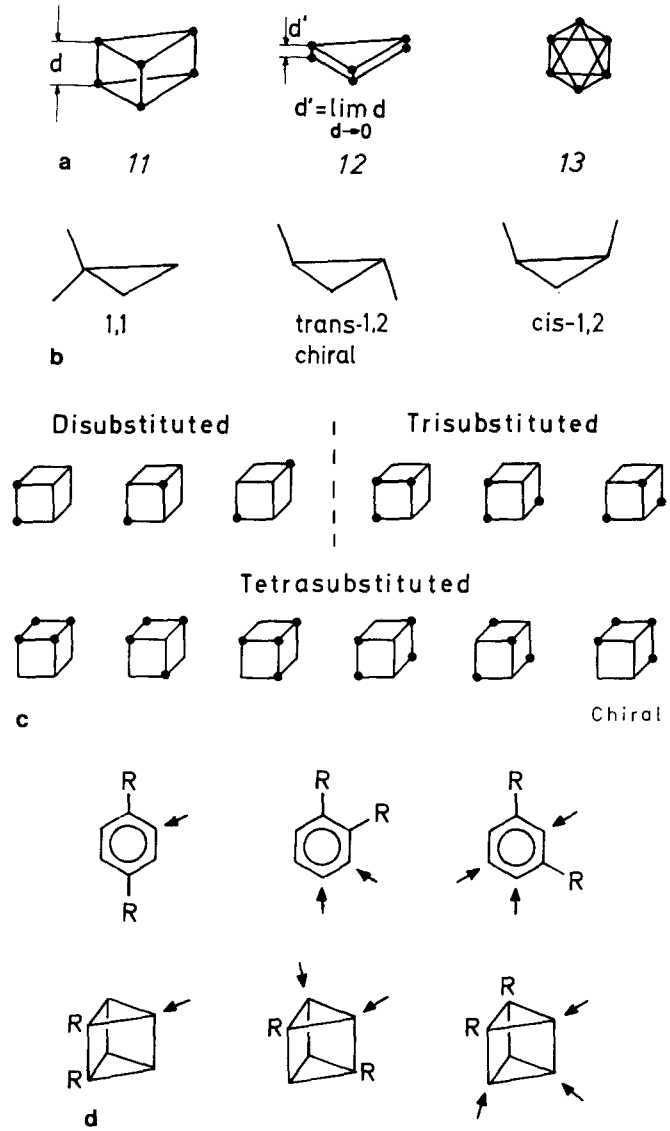


Fig. 6.

Indeed, there are four molecules if all types of stereoisomerism for dichlorocyclopropane are considered; if enantiomerism is ignored we are left with three isomers: 1,1; *cis*-1,2; and *trans*-1,2; finally, if we disregard stereoisomerism, only two constitutions remain, namely 1,1 and 1,2 [Fig. 6(b)].

Cubane (**1**) also presents stereoisomerism which can be taken into account or ignored. The two corresponding cycle indices and counting series are

$$Z(\mathbf{1}) = (x_1^8 + 8x_1^2x_3^2 + 9x_2^4 + 6x_4^2)/24,$$
$$\mathrm{ICS}(\mathbf{1}) = r^8 + r^7s + 3r^6s^2 + 3r^5s^3 + 7r^4s^4 + \cdots,$$
$$Z'(\mathbf{1}) = (x_1^8 + 6x_1^4x_2^2 + 8x_1^2x_3^2 + 13x_2^4 + 12x_4^2 + 8x_2x_6)/48,$$
$$\mathrm{ICS}'(\mathbf{1}) = r^8 + r^7s + 3r^6s^2 + 3r^5s^3 + 6r^4s^4 + \cdots.$$

The mono-, di-, and tri-substituted cubanes are all achiral, but one of the six tetrasubstituted cubane constitutions is chiral; this accounts for the difference between the two counting series indicated above [Fig. 6(c)].

We end this chapter by mentioning two relevant items of historical interest, linked with the symmetry of substituted benzenes.

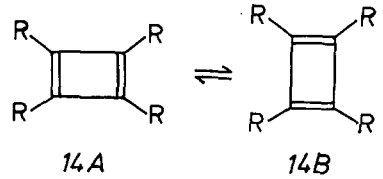
(i) The polemic between Kekulé and Ladenburg about the hexagonal and the benzprismane formulas, respectively, was based on the fact that both structures give rise to the same numbers of constitutional isomers for mono-, di-, trisubstituted systems, etc. This is a consequence of the fact that the two graphs have the same cycle index $Z(G)$, i.e. the two structures are coisomeric[65b]. Only later did Baeyer bring conclusive evidence for the Kekulé formula which (a) is strain-free, (b) gives the right pattern for *ortho*-substitution (see below), which must be vicinal as is known from the formation of phthalic anhydride, and (c) does not lead to enantiomers in agreement with the facts, and in opposition to Ladenburg's formula.

(ii) Körner's "absolute method" for assigning *ortho*(1,2), *meta*(1,3), and *para*(1,4) structures to benzenes with two identical substituents R is based on their conversion into trisubstituted compounds as follows: *para* → 1,2,4 (one compound); *ortho* → 1,2,3 + 1,2,4 (two compounds); *meta* → + 1,2,3 + 1,2,4 + 1,3,5 (three compounds, irrespective of the relative amounts), according to the symmetry axes of the initial disubstituted systems. It can be observed that Ladenburg's "ortho"-disubstituted benzprismane which leads to three tri-substituted derivatives is not vicinal [Fig. 6(d)].

JAHN–TELLER EFFECTS

In 1937, Jahn and Teller showed that for a nonlinear molecule or ion, a situation of orbital degeneracy cannot be stable, and the molecule or ion will distort in such a way as to break the degeneracy due to symmetry.

The cyclobutadiene molecule which is antiaromatic illustrates this effect: the geometry of the ground state is rectangular, but the bond shift through a symmetrical square excited state takes place rather easily, as demonstrated by Carpenter *et al.*[66], Masamune *et al.*[67] and Mayer *et al.*[68]; Carpenter[66] argued that there must exist a quantum-mechanical tunneling[69] for the intramolecular bond shift despite the fact that the CR groups in cyclobutadiene [CBD, Fig. 7(**14**)] are heavy (the effect was studied with R = H and D); they travel a very short distance, about 0.2 Å, during the bond-shift reaction (**14A**) ⇌ (**14B**). Calculations had indicated that the square antiaromatic CBD is unstable relative to a second-order Jahn–Teller distortion, leading to a singlet rectangular ground state[70].



14A *14B*

Fig. 7.

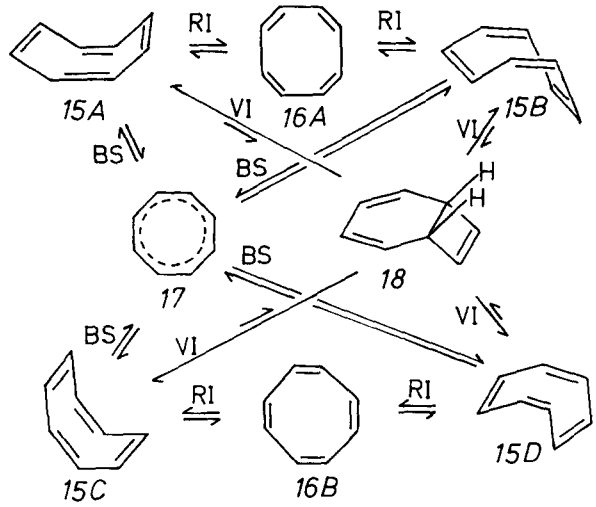


Fig. 8.

A similar process occurs in cyclooctatetraene [COT, Fig. 8(**15**)]. This molecule is, however, nonplanar (tub shaped) so that, in addition to bond-shift (BS) process, ring-inversion process (RI) also occur. The activation energies for these processes were measured by Paquette *et al.*[71] for substituted, and by Anet for unsubstituted, COT[72].

For the ring-inversion (**15A**) $\rightleftharpoons$ (**15B**) or (**15C**) $\rightleftharpoons$ (**15D**) a very low activation barrier ($\Delta G^{\ddagger}$ = 9.5 kcal/mol) was measured; the transition state is the planar localized molecule (**16A**) or (**16B**), respectively. For the bond-shift reactions (**15A**) $\rightleftharpoons$ (**15C**) or (**15B**) $\rightleftharpoons$ (**15D**) the transition state is the planar antiaromatic (delocalized) molecule (**17**) and the activation barrier $\Delta G^{\ddagger}$ = 13.3 kcal/mol.

The difference between these two values is in good agreement with the Dewar resonance energy (−4 kcal/mol) calculated by Dewar and Gleicher[73]. In sterically congested or chiral COT derivatives (1,3- or 1,4-di-*t*-butyl- and 1,3,5,7- or 1,2,3,4-tetramethyl-COT) the BS activation barriers increase enormously, attaining 35 kcal/mol, but the difference $\Delta H^{\ddagger}_{RI} - \Delta H^{\ddagger}_{BS}$ remains practically constant between −3.4 and −5.4 kcal/mol.

For the valence isomerization (VI) to the bicyclic isomer (**18a**) a much larger activation barrier was determined by Vogel *et al.*[75] and by Huisgen *et al.*[74], namely about 28 kcal/mol.

There exists at present an ongoing debate about the hydrogen bond in β-diketones: is the proton centered [Fig. 9(**19**)] or oscillating [(**20A**) $\rightleftharpoons$ (**20B**)]? Many facts are included in an excellent recent review[76].

A somewhat related problem concerns the onset of bond alternation in Hückel-type [4*n* + 2]-annulenes, predicted by Longuet-Higgins and Salem[77]. The fact that [18]-annulene (Fig. 10) has unequal bond lengths is due to its geometry and not to this electronic effect, as indicated by the fact[78] that the unequal bonds do not alternate (. . . *abab* . . .) but follow the symmetry of the molecule (. . . *abbabb* . . .) with bond distances a = 1.419 Å and b = 1.382 Å (for conversion to picometers, 1 Å = 100 pm).

However, it was found recently that in Nakagawa's tetra-*t*-butyl-bisdehydroannulenes (IUPAC tetradehydroannulenes) the polyene-chain bond lengths are equalized in the dehydro-[18]-annulenic system with m = 1, n = 4[79a] but they alternate in the dehydro-[22]-annulenic system with m = 2, n = 5[79b]; the number of π-electrons is $4n$ + 2.

On the other hand, the fact that $C_6N_6O_6$ has neither a structure of hexanitrosobenzene, nor

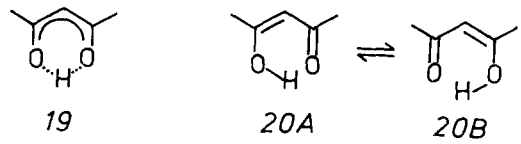


Fig. 9.

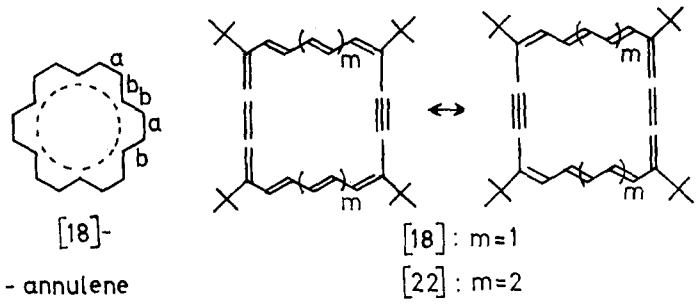


Fig. 10.

with each nitrogen atom being singly bonded to a carbon atom (both these structures would have sixfold symmetry), but rather the threefold symmetrical structure of benzotrifuroxan[79c] is probably due to the lower energy of the last structure relative to the two former ones, and not to the Jahn–Teller effect.

To quote again from Coulson[4b]:

> It is as if Nature said to us: "I have some important principles, and they do indeed dominate whole areas of chemistry, and of physics too. But I am subtle: I cannot always be treated as if I only had one idea in my head. You must use your experimental and theoretical tools carefully. Mother Nature has some feminine characteristics which from time to time will reveal themselves—perhaps to your discomfiture!"

In the field of metallic xomplexes, Jahn–Teller effects play an important role. Determinations of Jahn–Teller coupling constants for octahedral complexes are rationalized theoretically[80]. There also exist second-order Jahn–Teller effects, and pseudo-Jahn–Teller effects[80].

SYMMETRY OF LINEAR MACROMOLECULES

The geometrical single-strand helical symmetry of proteins adumbrated by H. Vasiliu[81] and demonstrated by Pauling and Corey, as well as the double helix structure discovered by Crick and Watson, are too well known to be mentioned more than cursorily here.

We shall discuss the symmetry in linear infinite polymer chains consisting of repeating units. An example is the stereochemistry of vinylic polymers resulting from regular head-to-tail polymerization of $H_2C=CHX$ (X = CH_3, Cl, Ph, OAc, etc.); the constitution is fixed but the stereochemical configuration of each –CHX– group may be either R or S. An isomorphic problem arises when considering the constitution of binary copolymers formed from two monomers, say R and S.

The repeating unit in the simplest case is R (isotactic vinylic polymers, or homopolymer R without incorporation of the second comonomer). The next higher case is of repeating units RS (syndiotactic vinylic polymer, or alternating copolymer). Most textbooks do not consider any further situation, although present-day NMR spectrometric methods "see" beyond the dyad regularity, namely one may observe heterotactic triads (. . . RRSRRS . . .), various tetrads, etc. A systematic enumeration of such possibilities is presented in Table 1. In order to avoid repetitions or duplications, the number of R configurations/monomers is considered to be equal to, or higher than, that of S counterparts, and the sense in which one goes along the chain is arbitrary; therefore RRS is considered to include RSS by the R/S reversal, whereas RSRRS is considered to include both RSRRS (in the opposite sense of going along the chain) and RSSRS (by R/S reversal).

Interestingly, for a given number n of monomer molecules in the repeating unit, the number N of solutions is seen to form the Fibonacci sequence ($F_i = F_{i-1} + F_{i-2}$) for $n \leq 8$ (but not for higher n values):

$$N_n = F_{n-2} \quad \text{with } F_0 = F_1 = 1.$$

Table 1. Linear infinite chains of binary copolymers and the number N of discrete solutions in terms of repeating units which are irreducible to solutions with lower n (where n is the number of monomer molecules in the unit)

n	Chain	Unit	N	n	Unit	N
1	. . . RRRRRR . . .	R	1	6	RRRRRS RRRRSS RRRSRS RRRSSS RRSRSS	5
2	. . . RSRSRS . . .	RS	1			
3	. . . RRSRRSRRS . . .	RRS	1			
4	. . . RRRSRRRS . . . . . . RRSSRRSS . . .	RRRS RRSS	2	7	RRRRRRS RRRRRSS RRRRSRS RRRSRRS RRRRSSS RRRSRSS RRSRRSS RRSRSRS	8
5	. . . RRRRSRRRRS . . . . . . RRRSSRRRSS . . . . . . RRSRSRRSRS . . .	RRRRS RRRSS RRSRS	3			

Earlier connexions between Fibonacci numbers and chemistry were observed in enumerating Kekulé structures and in other theoretical problems: the numbers of Kekulé structures for [n]-helicenes or other catacondensed benzenoid aromatic hydrocarbons without any anthracenic (linearly) condensed portion from the Fibonacci sequence[82].

Table 1 may be translated in the binary enumeration system. The analogous problem for ternary copolymers corresponds to enumerating different repeating patterns in the ternary enumeration system, and so on. A computer program was devised for compiling all these cases[83].

SYMMETRY AT THE SUPRAMOLECULAR LEVEL: CONSERVATION OF ORBITAL SYMMETRY, AND REACTIONS WITH AROMATIC TRANSITION STATES

The Woodward–Hoffmann rules[84] explain the stereochemistry and the allowed/forbidden character of concerted reactions (pericyclic reactions) which involve the cyclic permutation of σ and/or π electrons. These rules are therefore on the same fundamental level as those which explain why some thermodynamically allowed reactions do not occur in practice owing to electronic or steric factors.

Observations of several research groups[85–94] converged to show the fact that in thermal reactions pericyclic processes involving *three* electron pairs occurred easily; on the contrary, photochemical processes involving *two* electron pairs are favored. Evans[85] had formulated the hypothesis that reactions such as the Diels–Alder cycloaddition and its reversal (retrodiene ring-opening) proceed thermally because they have an aromatic transition state. Dewar[86] added to this the fact that photochemical $2\pi + 2\pi$ cycloadditions must have antiaromatic transition states.

Mathieu and Valls[92] reviewed all reactions with six-membered transition states known until 1956; Balaban[93] continued this review and included reactions which had not yet been observed but were theoretically possible.

Woodward and Hoffmann formulated their rules in the most general terms based on the idea that the frontier molecular orbitals [MOs; highest occupied, HOMO, and lowest unoccupied, LUMO] determine the course and stereochemistry of such reactions.

We shall exemplify by showing three related thermal processes: the Diels–Alder cycloaddition, the Cope rearrangement (a [3,3]-sigmatropic process) and the 1,5-hydrogen shift (a [1,5]-sigmatropic reaction) (Fig. 11).

The correlation diagram† for the Cope rearrangement and its transition state has the following constraints: (i) according to the symmetry element of the process (a plane for the boat-shaped transition state) electronic levels are symmetrical or antisymmetrical; (ii) in the correlation, no levels of the same symmetry may cross (noncrossing rule); (iii) the electronic oc-

†Correlation diagrams are not reproduced here because they are well known[84,90].

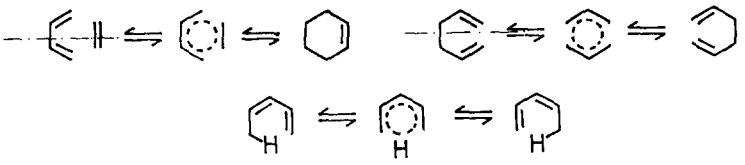


Fig. 11.

cupancy in the initial state is transferred to the transition state and the final state according to the correlation lines; and (iv) if the electronic occupancy of the transition state or final product corresponds to a higher-energy state, the reaction is forbidden, and it is allowed if the latter states have equal or lower energy than the initial state.

Correlation diagrams show that the Cope rearrangement and the $4\pi + 2\pi$ cycloaddition are thermally allowed; the former reaction is an automerization, and therefore could also be allowed photochemically, had the activation barrier for the first excited state lain lower in energy than the initial/final product (this is not the case). It is easy to see that in the Diels–Alder reaction the first excited state would have yielded the second excited state, so that this reaction is also forbidden photochemically. On the other hand, the $2\pi + 2\pi$ cycloaddition is photochemically allowed; the corresponding thermal reaction which would lead to a doubly excited state is strongly forbidden as a concerted reaction. It should be noted that in the latter case there are two symmetry elements (mutually orthogonal planes).

The stereochemical consequences of the Woodward–Hoffmann rules may be seen for the thermal electrocyclic reactions of 1,3-butadiene yielding cyclobutene and of 1,3,5-hexatriene yielding 1,3-cyclohexadiene. The symmetry element in a conrotatory process is a two-fold axis, while in a disrotatory process it is a symmetry plane; one can see that both processes are thermally allowed. If one constructs the correlation diagrams for a disrotatory (2 + 2)-process or a conrotatory (2 + 2 + 2)-process one can see that such processes are forbidden. Many known reactions have been thus rationalized; the few exceptions are probably due to the reactions proceeding in a totally nonconcerted fashion (actually Dewar maintains that no reaction may be exactly concerted). The topic is related to Pearson's rules[95] which are reviewed in more detail by Pearson in a previous issue.

For this reason, and because correlation diagrams are available in many books, the correlation diagrams pertinent to the above discussion have not been reproduced here.

REACTION GRAPHS; HEURISTIC SYMMETRY OF (3, γ)-CAGES; SYMMETRY IN HYPERSPACES E_3, E_4

Reaction graphs present all theoretically possible reactions occurring in a given system so as to enable chemists to choose the actual path followed during the course of the reaction. Vertices of a reaction graph are molecules or ions, and edges represent elementary reaction steps. The first reaction graph was published in 1966 to depict the degenerate rearrangement (automerization or topomerization) of ethylcarbenium ions with five different substituents[96]. If the two carbon atoms are distinguishable (e.g. by isotopic substitution) the reaction graph has 20 vertices and is called the Desargues–Levi graph [Fig. 12(**21**)]; if they cannot be distinguished, pairs of antipodal vertices became equivalent and the Petersen graph (**22**) results with ten vertices. In both cases the graph is cubic (regular graph of degree 3, where three lines meet at each vertex), because in each case there are three possibilities of rearrangement.

Interestingly, soon afterwards the same two graphs were published in another context, namely the pseudorotation of pentacoordinated phosphorus compounds or of other trigonal-bipyramidal molecules with five different ligands: the Desargues–Levi graph results when enantiomerism is taken into account[97] and the Petersen graph when it is disregarded[98]. Mislow[99] recognized that in both cases the substituents were grouped in a set of two and a set of three substituents; therefore the resulting graphs are isomorphic.

The Petersen graph occupies a privileged place in graph theory and is displayed on the cover of several books on graph theory[100,101]. Its "magic attraction" may be due to the relationship with the pentagram in the usual representation (**22**), and is probably connected with

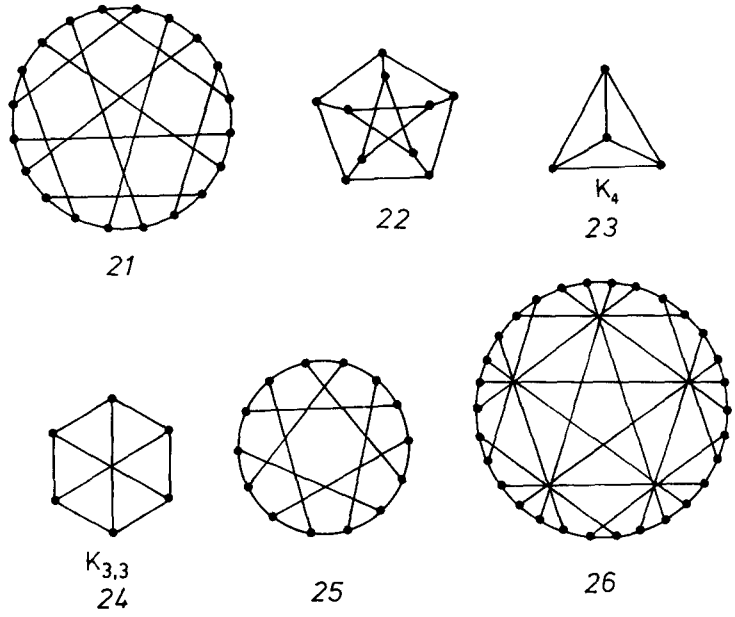


Fig. 12.

its high order of the symmetry group (though this is not readily apparent); this will be presented in more detail below when the cages will be discussed. The Petersen graph is the (3,5)-cage, so-called because it is the smallest cubic graph with girth $\gamma = 5$, i.e. the cubic graph with the smallest number of vertices wherein no cycle is smaller than 5-membered. The $(3,\gamma)$-cages were reviewed by Wong[102]. The (3,3)-cage is the tetrahedron graph K_4, (**23**) (4 vertices), the (3,4)-cage is the Thomsen graph ($K_{3,3}$), (**24**) with 6 vertices (one of the two graphs described by Kuratowsky in connection with his graph planarity theorem), the (3,6)-cage is the Heawood graph (**25**) (14 vertices), the (3,7)-cage is the McGee graph (24 vertices, vertex- and edge-intransitive), the (3,8)-cage is the Tutte graph (**26**) (30 vertices)[103] and the (3,12)-cage is the Benson graph (126 vertices)[104].

Balaban[105], and later O'Keefe and Wong, and Harries, described three (3,10)-cages with 70 vertices[106]. By observing relationships among the above cages (cages of even girth afford the next lower cage of odd girth by excision of a branched tree) Balaban removed a maximal branched tree from Benson's graph and obtained the conjectured unique (3,11)-cage with 112 vertices[107]. The same procedure, however, failed to yield the presumed (3,9)-cage but afforded instead a cubic graph with 60 vertices. About 30 other different graphs with 60 vertices and girth 9 were found by Balaban, Foster, Frucht, Biggs, Evans and Harries, but they were not the (3,9)-cage because Biggs and Hoare, and then Evans, found two smaller graphs of girth 9, having only 58 vertices[108]. The surprising fact about these two graphs is their very low symmetry. By analogy with all $(3,\gamma)$-cages so far known it can be conjectured that these are not the (3,9)-cages, and that one has to look for other cubic graphs of girth 9 with $\leqslant 58$ vertices.

Thus symmetry is a heuristic criterion for assessing whether a conjecture is likely to be true or false.

The symmetry of graphs is measured by the order of their automorphism group. Unlike the symmetry of polyhedra, which is apparent from their rotations/reflections, the symmetry of graphs must consider all permutations of edges because graphs must be viewed as floppy[109], not rigid, geometrical realizations of the abstract definition of graphs (a superposition of the nonempty set of vertices on itself), so that an edge is actually an unordered pair of vertices. As a consequence, graphs may have much higher symmetries than polyhedra, for comparable numbers of vertices and vertex degrees. Thus, the orders of the symmetry group $\Gamma(G)$ of the regular dodecahedron as a polyhedron, and of the Desargues–Levi graph (both are cubic graphs with 20 vertices) are 60 and 240 respectively. Table 2 presents in more detail the orders $\Gamma(G)$ of the automorphism groups of polyhedra and cages; the tetrahedron graph is the (3,3)-cage.

s-Unitransitive (s-regular) graphs were defined as graphs which have exactly one automorphism mapping any path of length s on any other path of the same length (but not for a

Table 2. s-Unitransitive or s-regular graphs with v vertices and girth γ

Polyhedra (geometrical objects) Denomination	v	s	$\Gamma(G)$	γ	(3,γ)-Cages (graphs) Graph	v	s	$\Gamma(G)$
Tetrahedron	4	2	12	3	K_4 (**23**)	4	2	24
Cube (**1**)	8	2	24	4	Thomsen $K_{3,3}$ (**24**)	6	3	72
Pentagonal prism	10	0	20	5	Petersen (**22**)	10	3	120
Dodecahedron	20	2	60	6	Heawood (**25**)	14	4	336
Truncated tetrahedron (**4**)	12	1	36	7	McGee	24	—	32
Truncated cuboctahedron (**7**)	48	0	144	8	Tutte (**26**)	30	5	1440

path of length $s + 1$). Vertex-transitive and edge-intransitive graphs such as the prisms are 0-uniregular; vertex- and edge-transitive graphs are 1-uniregular. The order of the automorphism group of an s-uniregular cubic graph with n vertices is $3n \times 2^{s-1}$[103].

The symmetry of reaction graphs for several automerizations was analyzed by Balaban, then Randić: the Petersen graph[96,104,105] and the Desargues–Levi graph[96,106] mentioned above, the homotetrahedryl cation automerization[113,114], and the automerization of tetragonal pyramidal complexes[115,116].

The graphs of the polyhedra have twice-higher orders of automorphism groups than those of the corresponding polyhedra because the steric configurations are defined for the polyhedra but undefined for their floppy graphs; thus, the graph K_4 of the tetrahedron has $\Gamma(G) = 24$, twice as much as for the tetrahedron as polyhedron.

An interesting problem is to speculate on how to visualize plastically the high symmetries of the cages. One can think of a game in which vertices are articulated mechanical devices, edges are colored flexible tubes with telescopically variable lengths, and the aim is to obtain the automorphisms maintaining the shape but varying the colours. Or one can think about a dynamical "sculpture" which automatically performs these automorphic interconversions.

An alternative idea is even more interesting: it is clear that all cages with $\gamma > 3$ in Table 2 are nonplanar graphs. The Thomsen graph $K_{3,3}$ with six vertices and the complete graph K_5 with five vertices can have no geometrical realizations in our tridimensional Euclidean space E_3 such that all edges and vertices are equivalent; however, in the four-dimensional space E_4 this is possible for the above two graphs: K_5 is the four-dimensional hypertetrahedron, which we may visualize as a tetrahedron whose four vertices are connected to a fifth vertex in E_4 exterior to E_3 where for convenience we represent the fifth vertex embedded *inside* the tetrahedron [because we cannot see another point equidistant to the other four and equivalent to them, just as the people in E. A. Abbott's *Flatland*[110] cannot represent a tetrahedron other than as a flat K_4 (**23**)]. $K_{3,3}$ is to be viewed as a bipartite graph with a set V_1–V_3 of three disconnected vertices at the corners of equilateral triangle; they are connected to a set v_1–v_3 of three disconnected vertices. Now, if v_1 and v_2 occupy equivalent positions above and below the plane of V_1–V_3, the last vertex v_3 must be in a place in the fourth dimension so as to be equivalent to v_1 and v_2 and form with them an equilateral triangle, and to be at the same time equidistant from V_1–V_3 (Fig. 13). Again we have to put up with our "three-dimensional Flat-landness," and to project conventionally vertex v_3 from the fourth dimension into the centre of the figure. The

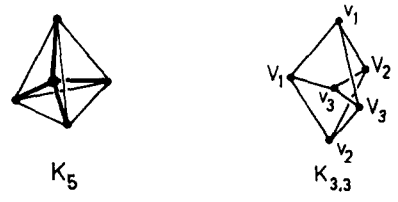


Fig. 13.

resulting object should have six equivalent vertices and nine equivalent edges, but we can only visualize their projections in our three-dimensional space.

It is quite easy to see that for a two-dimensional Flatlander the edges and vertices of K_4 on a plane are not equivalent, yet we know that the tetrahedron has equivalent vertices and edges. We can therefore easily see that a similar equivalence holds in the fourth dimension for K_5. It is, however, more difficult to see the equivalence of vertices and edges in $K_{3,3}$, but after some thought and imaginative effort one realizes the beautiful symmetry of the smallest nonplanar cage from Table 2 in the multidimensional space. It is an open question whether for the other cages from Table 2 it will be enough to go to E_4, or higher (E_5, etc.) for imagining "objects" displaying the equivalence of vertices and edges, which surpasses by far in richness (and beauty?) the same kind of equivalence in polyhedra.

The fascination exerted on the human mind by the five regular polyhedra is associated with the equivalence (i.e. transitivity) of vertices and edges and faces. We quote from Coxeter's book[118]: "Sir D'Arcy W. Thompson once remarked to me that Euclid never dreamed of writing an Elementary Geometry: what Euclid did was to write a very excellent (but somewhat long-winded) account of the Five Regular Solids, for the use of Initiates." It is appropriate to recall within the context of symmetry the fascinating book *On Growth and Form*[119].

On the applied side, Buckminster Fuller's idea of the geodesic dome has been elaborated rigorously from first principles by Emde (Darmstadt) who proposed an interesting 4×4 square matrix for characterizing any homogeneous polytope[120].

What artist will find a means of making visible or palpable to the senses rather than to the mathematically trained mind the tremendous 5-unitransitivity of the Tutte graph, or of other highly symmetrical graphs? If he or she succeeds, another step will be taken along the path described by Hermann Weyl: "Symmetry, as wide or as narrow as you may define its meaning, is one idea by which man through the ages has tried to comprehend and create order, beauty, and perfection"[5].

SPHERES AND CHEMISTRY

Most people will agree that the most symmetrical object in our world is the sphere; indeed, any movement which conserves its center is an automorphism, and there is an infinity of such moves. It may seem difficult to imagine something with a higher symmetry, yet this can be done. If one thinks about the circle and the sphere, then the reply is obvious. Since the sphere has one extra degree of freedom corresponding to its three-dimensionality (3D) relative to the circle, the reply is a 4D-hypersphere. Of course, Cantor showed that the intuitively obvious is out of place when discussing infinities, but this is an opportunity to discuss N-dimensional (ND hyperspheres. We shall denote by A_N the $N-1$ dimensional content, and by V_N the N-dimensional content, of the ND-hypersphere (e.g. for $N = 3$ the area A_3 and the volume V_3 of the sphere; for $N = 2$, the perimeter A_2 and the surface V_2 of the circle). We recall the recurrences[118] where R is the radius:

$$A_{N+2} = 2\pi NR^2 A_N = 2\pi R V_N,$$

and we obtain therewith Table 3.

Is there any connexion between spheres and chemistry? Yes, indeed, and we shall mention two such connexions.†

Table 3. The N- and $(N-1)$-dimensional content of the ND-hypersphere

N	1	2	3	4	5
V_N	$2R$	πR^2	$4\pi R^3/3$	$\pi^2 R^4/2$	$8\pi^2 R^5/15$
A_N	2	$2\pi R$	$4\pi R^2$	$2\pi^2 R^3$	$8\pi^2 R^4/3$

†A third one is also well known: the two possible types of close packing of equal spheres corresponding to the cubic and the hexagonal closest packings[39].

(1) The "gear effect" of three-pronged substituents such as alkyl groups was demonstrated by Roussel, Metzger, and coworkers[121]. Unlike a halogen substituent, whose Van der Waals "envelope" is spherical, a methyl or an isopropyl group are pronged so that their intramolecular rotation angle changes the free energy of the molecule. There exists a lowest energy conformation where vicinal substituents are geared like cogwheels. The topic was the subject of some controversies[122], and was recently reviewed[123].

(2) The spontaneous formation of bilayer vesicles from surfactant molecules on ultrasonic dispersion in water is a "membrane mimetic chemistry"[124]. The surfactant, like the biological constituents of membranes or of liposomes, must have two long tails (nonpolar alkyl chains) and a polar ammonium or phosphate headgroup. The spherical structure of the vesicle can be frozen by photochemical or radical-initiated polymerization if one uses surfactants with double bonds in the tail chains or attached to the head group. Interestingly, many membrane studies using spin labels are made with "erythrocite ghosts" (red blood corpuscles whose hemoglobin content has been removed); in such cases it is possible to know whether the sphere conserves its initial structure or has been turned inside out.

This brings us to the conclusion of this paper, which raises some problems on the topology of N-dimensional objects. A Flatlander cannot visualize a Möbius band or a Klein bottle [Fig. 14(a)-(**27**)], and Escher's ants crawling across the Möbius band [Fig. 14(b)] illustrate this point (it would have better suited our purpose if the band had been opaque and much larger, and the ants much flatter). Now, thinking about Plato's reflections about the shadows that we see on the walls of our cave, and about the modelling of the real world after these shadows, let us imagine (if we can) four-dimensional analogs of a Möbius band and of a Klein bottle (which are 3D projections of the 4D objects), as well as other topological oddities which have no counterpart in our three-dimensional world.

A being in a 4D world would be able to see at the same time the exterior and the interior of a sphere, both of which are open towards the fourth dimension, just as the circle is open to a 3D being like us but is a closed to a coplanar Flatlander. Thus we end with another limerick:

A mathematician named Klein
Thought the Möbius bands were divine.
Said he, "If you glue
The edges of two
You'll get a weird bottle like mine.

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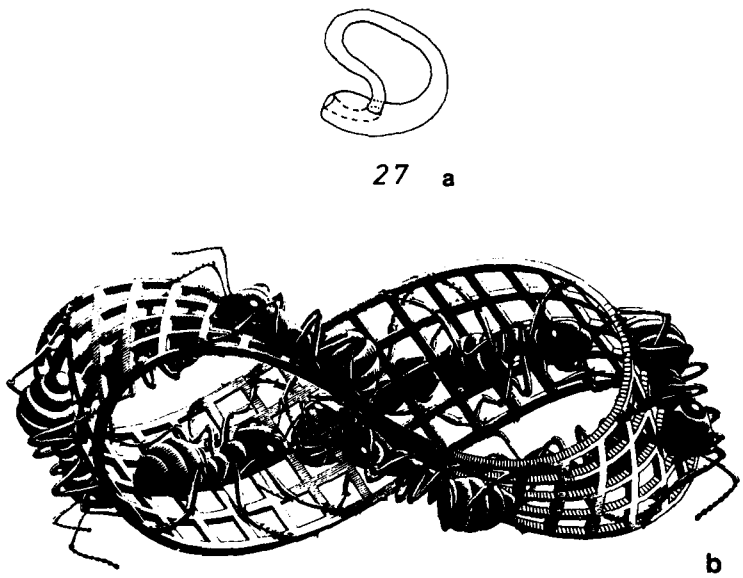

Fig. 14. (© M. C. Escher Heirs c/o Cordon Art, Baarn, Holland).

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